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CHARACTERIZATION OF THE PORE STRUCTURE OF STARCH BASED FOOD MATERIALS

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Abstract

Macroscopic pore structure parameters (bulk density, true density and porosity) and microscopic pore structure parameters (percentage closed pore volume and pore size distribution) for a highly expanded type (Wonder White Sandwich Bread) and a relatively compact type (Chessmen Butter Cookies) starch based food material were determined and their pore structures were compared. Bulk density determined by solid displacement and true density determined by pycnometry yielded porosity measurements of 0.9 for bread and 0.6 for cookies. Percentage closed pore volume calculated by comparing the true density of porous samples of bread and cookies with the true density of their compacted pellets showed that both bread and cookies contained closed pores. Pore size distributions representative of the mercury porosimetry range (pores less than 200 μm in diameter) indicated that the smallest pore diameter was 6 μm for both bread and cookies. Pore size distributions obtained corresponded to about 16% and 65% of the total pore volume in bread and cookies, respectively. Both bread and cookie samples were found to undergo capillary hysteresis. Unidimensional mercury intrusion studies revealed a highly interconnected pore structure both in bread and cookies. Scanning electron microscopy (SEM) photomicrographs used to evaluate the pore structure qualitatively showed no directional orientation of the pore structure.

Key Words: Starch based foods, porous media, mercury porosimetry, pycnometry, porosity, pore size distribution, cookies, bread, image analysis, scanning electron microscopy.

Introduction

Starch based food materials are puffed, extruded or baked grain products with a pore volume of 60-90% or even higher (Barrett and Ross, 1990; Barrett et. al., 1990). Filling in the available pore space with a high calorie liquid food material will thus yield a higher calorie food product in a relatively low bulk volume. Filling in the pores of starch based porous food materials with high calorie liquid foods is called "infusion". Infusion is a capillary penetration process in which the infusing liquid rises in the capillaries of the starch based porous food material until it fills up the available pore space. Pressure required for capillary penetration is dictated by both the characteristics of the infusing liquid (Hiçşmaz, 1990) and the pore size of the starch based solid matrix. Moreover, high calorie liquid foods usually contain suspended particulate material such as cocoa particles in chocolate syrup. Thus, to obtain uniformly infused final products (Barrett and Ross, 1990; Barrett et. al., 1990), pore sizes of starch based solids should always be considerably larger than the particle size of the particulate solids in the infusing liquid. In addition, the qualitative make up of the void space is important in choosing an effective solid matrix with desired interconnectedness of the pore structure. Void spaces in porous solids are formed by three types of pore structures; (a) interconnected pore segments, (b) isolated or noninterconnected pore segments and (c) dead-end or blind pore segments (Fig. 1). Interconnected pores are accessible on both ends, blind pores are accessible only on one end, while noninterconnected pores are inaccessible closed pores within the solid material and behave as a part of the solid (Dullien, 1979). Since closed pores are inaccessible, they decrease the available pore space for infusion. Therefore, in order to develop a concept about the pore structures of commercially

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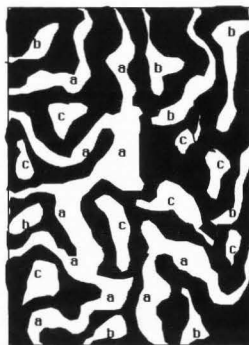


Fig. 1. Schematic representation of types of pores making up the pore space:
(a) Interconnected pore space
(b) Dead-end or blind pores
(c) Noninterconnected or closed pores.

available starch based porous food products, a highly expanded material (Wonder White Sandwich Bread) and a relatively compact material (Chessmen Butter Cookies) were selected for this study. Macroscopic pore structure parameters (bulk density, true density and porosity) and microscopic pore structure parameters (percentage closed pore volume and pore size distribution) were investigated for both materials and compared. Also, variability among different samples of bread and cookies was assessed.

Review of Methods for Measuring the Pore Structure Parameters

There exist various methods to measure porosity, including direct, optical, imbibition, mercury injection, gas expansion and density (Scheidegger, 1974). Optical methods using photomicrography give rather qualitative results on interconnectedness of the pore structure (Dullien, 1979). Direct methods, the imbibition method and the mercury injection method, are destructive techniques which do not allow the sample to be used for further testing. In this study, the bulk density of porous samples was measured by the solid displacement technique, while the true density was measured by the gas expansion method known as pycnometry. These are nondestructive methods which allow the samples to be used for further testing. In the food industry, pycnometry is used to characterize cereal products such as

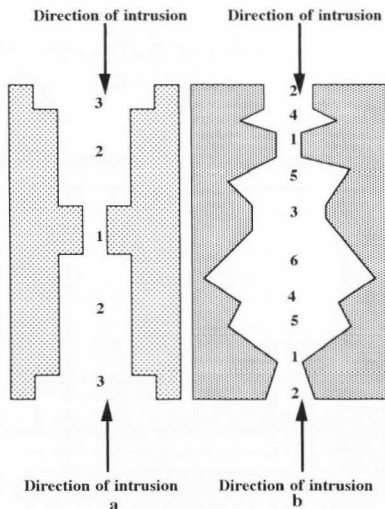


Fig. 2. An illustration of porous medium (capillary segments are numbered in the order of increasing diameter)
(a) represented by a hypothetical straight capillary channel
(b) represented by an actual pore channel.

flakes and muesli (Climas, 1987) and grain kernels (Chang, 1988).

Volume based pore size distribution is the probability density giving the distribution of pore volume with respect to particular pore sizes (Dullien, 1979). In this study, classical mercury porosimetry which utilizes the straight capillary approach was used to predict the pore size distributions. The straight capillary approach assumes the porous medium to be made up of a straight bundle of capillaries having various diameters, in which large pore segments are always followed by smaller ones (Fig. 2a). Thus, this type of modeling cannot predict capillary hysteresis which arises from the random distribution of large and small capillary segments (Fig. 2b). This happens because intrusion starts when the capillary pressure is enough for mercury to penetrate the #2 capillary segment which also flows into the #4 capillary segment, since the diameter of the #4 segment is larger than that of the #2 segment (Fig. 2b). In the same manner, when the capillary pressure is sufficient for intrusion into the #1 capillary

segment, #3-6 capillary segments are also intruded. On the other hand, during extrusion, #1 capillary segments empty into #4 and #5 (Fig. 2b) segments. Then, when the pressure decreases enough for the #2 capillary segments to be emptied, mercury is entrapped in #4 and #5 capillary segments, since these cannot empty into #2 and #1 segments at this capillary pressure (Dullien, 1979). Thus, the intrusion and extrusion curves are not superimposed. However, in the case of the straight capillary channel (Fig. 2a), hysteresis is not observed, since capillary segments with larger diameters are followed by capillary segments with smaller diameters.

Volume of mercury intruded vs. capillary pressure and pore entry radius can be interpreted in several ways such as volume based, surface area based and number based pore size distributions. Among those, only the volume based pore size distribution is meaningful for materials which undergo capillary hysteresis (Hiçşazmaz, 1990). Surface area based and number based distributions for such materials become meaningful by further modeling of mercury porosimetry data using network analogs (Batra et al., 1970; Dodson et al., 1971; Simon and Kelsey, 1971; Dullien and Azzam, 1973; Dullien and Dhawan, 1975; Sheffield and Metzner, 1976; Chatzis and Dullien, 1977; Azzam and Dullien, 1977; Dullien et al., 1977; Neira and Payatakes, 1978; Dullien, 1979; Deiber and Schowalter, 1979; Androustopoulos and Mann, 1979; Payatakes et al., 1980; Lapidus et al., 1985; Li et al., 1986).

In the food industry, pore size distributions employing the straight capillary model are used in the characterization of powders and grain kernels (Climas, 1987; Chang, 1988).

Materials and Methods

Materials

Wonder White Sandwich Bread (ITT Continental Baking Co.) was selected as the highly expanded starch based product and Chessmen Butter Cookies (Pepperidge Farms) was selected as the relatively compact material to be studied. Their compositions are given in Table 1. The reason for using commercial brands instead of making experimental bread and cookies is that the final scope of this study was to investigate the infusion characteristics of commercially available baked products. The main consideration in selecting these porous solid food materials was to investigate whether there is a difference with respect to the presence and quantity of closed pores, the smallest pore size and the pore size distribution characteristics between a highly expanded and a relatively compact

Table 1. Composition of cookies and bread as percentage on dry basis.

	Protein	Fat	Carbohydrate	Others
Cookies	6.4	17.7	74.2	1.7
Bread	11.6	4.3	67.5	16.6

starch based commercially available food product. Another consideration was a practical one: the possibility of obtaining rectangular samples with easily measurable dimensions. Dried bread and cookie samples easily fulfilled this requirement.

Preparation of the Starch Based Solids

Each package of bread yielded about twenty slices and twenty butter cookies were found in each pack. Different number of samples were used for different purposes and samples of various dimensions were prepared according to the requirements of each test and limitations of the equipment used. Care was taken to prepare samples from different slices so as to be able to assess slice-to-slice variations. In order to assess uniformity among samples with respect to porosity and percentage of closed pore volume, both samples with identical dimensions ($0.04 \times 0.06 \times 0.01 \text{ m}^3$ samples of bread and $0.05 \times 0.06 \times 0.006 \text{ m}^3$ samples of cookies) and samples with different dimensions (in a weight range of $0.5 \times 10^{-3} - 5.0 \times 10^{-3} \text{ kg}$ for bread and $1.0 \times 10^{-3} - 10.0 \times 10^{-3} \text{ kg}$ for cookies) were prepared. Five samples with identical dimensions from each material were tested, while fifteen samples of each material with different dimensions were used. The coefficient of variance obtained among samples used for each specific purpose are given in the "Results and Discussion".

Bread slices were dried in a convection oven (Precision Scientific Co.) at 65°C for three hours and then reduced to the desired sample sizes with the help of a Hamilton Beach electric knife. Cookies were reduced to the desired sample sizes without predrying. The surfaces of the cut samples were polished by fine sand paper so as to provide smooth surfaces, especially required for Scanning electron microscopy (SEM) and porosimetry tests. Cut samples were dried at 65°C for 72 hours. Preliminary experiments showed no additional moisture loss after this length of time.

Drying could have changed the pore size, but the ultimate aim, infusion, is a vacuum process (Hiçşazmaz, 1990) in which obtaining the necessary vacuum requires predried solid materials. Moreover,

drying is not expected to effect the pore structure of cookies, since cookies are originally quite low in moisture content (4.5% moisture). However, with bread, an originally high moisture content (40% moisture) material, drying may have affected the pore sizes.

Preparation of Bread and Cookie Pellets

In order to be able to calculate the percentage of closed pore volume in porous bread and cookie samples, it was necessary to measure the density of solids making up the bread and cookies. For this purpose, fine powders of bread and cookies were obtained and pressed into pellets with very low porosity when compared to the high porosity original bread and cookie samples. Bread and cookies were dried at 65°C for 72 hours in order to minimize sticking and clumping during comminution. Then, they were comminuted by using a Model M, Series 17 Comminuting Machine (W. J. Fitzpatrick Co.). The machine was equipped with a screen such that the largest particle size that went through was 48 mesh. The pellets were prepared

from 1×10^{-3} kg of the comminuted starch based solid by using a pellet mold and a hydraulic press (Pasadena Hydraulics Inc.). The hydraulic press used was equipped with a 0.1 m diameter ram which provided 4.5 kN/ full ram movement. Its range was 180 kN. Selected starch based solids were pressed at 45 kN producing perfect cylindrical shaped pellets. These pellets were kept at 65°C for at least 72 hours before testing. The bread and cookie pellets were 1.3×10^{-2} m in diameter and 7.0×10^{-3} m in height corresponding to a bulk volume of approximately 9×10^{-7} m³. True density of cookie pellets was measured as 1600 kg/m³, while the true density of bread pellets was 1300 kg/m³. The porosities of bread and cookie pellets were calculated as 0.03.

Determination of Bulk Density

Bulk densities of selected starch based porous solid food products were determined by the solid displacement technique using rapeseeds. A calibrated 0.14 m³ glass container was used. First, the tapped bulk density of rapeseed was determined by filling the glass container uniformly with rapeseeds through three tappings and smoothing the surface using a sharp razor blade. The bulk density was determined by dividing the weight of rapeseeds by the volume of the container. The arithmetic mean of ten measurements yielded a bulk density of 640 kg/m³ for rapeseeds. The bulk density of porous samples of bread and cookies with measured weights was determined by placing a sample in the glass container, filling it with rapeseeds and measuring the total weight so as to find the weight of

rapeseeds displaced by the sample. Then, knowing the bulk density of rapeseeds, the volume occupied by rapeseeds was calculated, thus yielding the volume of the solid sample and its bulk density. The arithmetic mean of five measurements was taken as the bulk density for a given sample.

Determination of True Density

True densities of bread and cookie samples were determined by the gas expansion method. In this method, the porous sample is enclosed in a container of known volume under a known gas pressure. The sample chamber is connected to a second chamber of known volume. When the valve connecting the two chambers is opened, the gas under pressure expands into the second chamber. Thus, the volume of solids can be calculated from the ideal gas law as;

$$V_s(P_1 - P_2) = V_1(P_1 - P_2) - P_2V_2 \quad (1)$$

where, V_1 is the volume of the sample chamber (m³), V_2 is the volume of the second chamber (m³), P_1 is the initial pressure (Pa), P_2 is the final pressure (Pa) and V_s is the volume of solids (m³). Since the bulk volume has already been determined by solid displacement, porosity of the sample can be calculated as;

$$\epsilon = \frac{V_B - V_s}{V_B} = \frac{\rho_B - \rho_s}{\rho_B} \quad (2)$$

where, ρ_B is the bulk density (kg/m³), ρ_s is the true density (kg/m³), V_s is the solid volume (m³) and V_B is the bulk volume (m³).

A QUANTACHROME stereopycnometer was used for true density measurements. This instrument was equipped with two sample cells, 1.56×10^{-4} and 3.42×10^{-5} m³. The expansion chamber of the pycnometer had a volume of 8.71×10^{-5} m³ as supplied by the manufacturer. The maximum pressure allowed in the sample chamber was 1.4×10^5 Pa and pressurization was achieved by using nitrogen gas. Tests were carried out between 1.10×10^5 – 1.24×10^5 Pa. Solid volume measurements for each porous sample of measured weight and bulk density were carried out in three replicates using the pycnometer, and the arithmetic mean of these three measurements was taken as the solid volume of the sample.

Determination of Percentage (%) Closed Pore Volume (Vol.)

Percentage closed pore volume was determined by comparing the true density of porous bread and cookie samples measured using the pycnometer with the true density of bread and cookie pellets as;

$$\text{True solid vol.} = \frac{\text{Sample weight}}{\text{Pellet true density}} \quad (3)$$

$$\begin{aligned} \text{Vol.} &= \text{Solid vol.} - \text{True solid} \quad (4) \\ \text{closed} & \quad \text{porous sample} \quad \text{vol.} \\ \text{pores} & \quad \text{determined by} \\ & \quad \text{pycnometry} \end{aligned}$$

$$\begin{aligned} \text{Total} &= \text{Bulk vol.} - \text{True solid} \quad (5) \\ \text{pore} & \quad \text{porous sample} \quad \text{vol.} \\ \text{vol.} & \end{aligned}$$

% closed

$$\begin{aligned} \text{pore} &= \frac{\text{Vol. closed pores}}{\text{Total pore vol.}} \times 100 \quad (6) \\ \text{vol.} & \end{aligned}$$

SEM Photomicrographs

Since the samples were dry, no special fixing procedure was used in their preparation for SEM. They were made conductive by sputter coating the surface with gold. The sections were prepared so that it would be possible to study the differences in pore structure among the inside and the top and bottom skins of cookies. With bread, no such differences were expected, since the test samples were cut from bread slices and were without skin. Another consideration in preparing the SEM samples was to observe directional differences in pore structure. Therefore, dried samples were considered as 3-dimensional (3-D) entities and sections were cut so as to expose the inner pore structure in x-, y- and z-directions. Twenty photomicrographs for cookies (five for the cookie skin, five in each of the x-, y- and z-directions exposing the inner structure in these directions) and 15 photomicrographs for bread (five in each of the x-, y- and z-directions exposing the inner structure in these directions) were taken. The clearest SEM representations for bread samples was obtained at 45X magnification. Higher magnifications showed only single pores. To make comparisons with bread, some cookie photomicrographs were also taken at 45X, but 100X was used for a general view, and a more detailed picture was obtained at 200X. The pore sizes in the photomicrographs were measured by taking the largest dimension of the pores as the pore diameter.

Mercury Porosimetry

Volume based pore size distribution of the bread and cookie samples were determined by mercury porosimetry. In principle, mercury porosimetry provides data on the increase in mercury-filled pore volume corresponding to a differential increase in the pressure gradient which can then be converted to the pore entry radii by the Laplace-Young

equation (Dullien, 1979) as;

$$P_c = \frac{2\sigma \cos\theta}{R} \quad (7)$$

where P_c (Pa) is the capillary pressure recorded by the porosimeter, σ is the surface tension of mercury (480×10^{-3} N/m), θ is the contact angle of mercury (140 degrees) and R (m) is the mercury filled capillary radius corresponding to that capillary pressure. Pore size distributions predicted by employing the Laplace-Young equation only, use the straight capillary approach.

The volume based pore size distribution was obtained as; dV/dP_c vs. R where dV/dP_c is the slope of intruded volume vs. capillary pressure data (Dullien, 1979; Winslow, 1984). The volume based pore size distribution function, $D_v(R)$, which is defined as the change in volume per unit interval pore radius is;

$$D_v(R) = \frac{dV}{dP_c} \frac{dP_c}{dR} = \frac{dV}{dR} \quad (8)$$

Moreover, the Laplace-Young equation indicates that;

$$\frac{dP_c}{dR} = - \frac{P_c}{R} \quad (9)$$

provided that the surface tension and the contact angle are constant. Thus;

$$D_v(R) = - \frac{P_c}{R} \frac{dV}{dP_c} \quad (10)$$

A QUANTACHROME AUTOSCAN 500 porosimeter equipped with a recorder and a microcomputer was used to determine the pore size distributions. The porosimeter used was capable of detecting pore sizes smaller than 200 μm . The full range of the porosimeter was adjusted to 3.45×10^5 Pa. Vacuum from the sample cell was pulled by a roughing pump which drew down to 6.6 Pa vacuum. The microcomputer received pressure vs volume data from the porosimeter, and the diameter intruded corresponding to each pressure was automatically calculated. Also, the volume based pore size distributions were automatically calculated. Data were normalized with respect to sample weight so as to provide comparisons among samples. In addition to those values, the median and mean pore diameters of the distribution function were calculated automatically as well. During the pore size distribution experiments, both intrusion and extrusion data were recorded

Table 2. Bulk density, apparent true density and porosity for $0.05 \times 0.06 \times 0.006$ m³ samples of butter cookies.

	Maximum	Minimum	Mean	C.O.V.* (%)
Bulk density (kg/m ³)	600	570	580	1.9
Apparent true density (kg/m ³)	1350	1290	1310	2.0
Porosity	0.56	0.54	0.55	1.6
Weight (kg)	9.2×10^{-3}	8.0×10^{-3}	8.5×10^{-3}	5.5

* C.O.V. : Coefficient of variance

** Apparent true density includes closed pore volume

Table 3. Bulk density, apparent true density and porosity for $0.04 \times 0.06 \times 0.01$ m³ samples of white bread.

	Maximum	Minimum	Mean	C.O.V.* (%)
Bulk density (kg/m ³)	140	120	130	6.7
Apparent true density (kg/m ³)	1340	1390	1370	1.5
Porosity	0.91	0.90	0.90	9.8
Weight (kg)	3.4×10^{-3}	2.8×10^{-3}	3.1×10^{-3}	5.5

* C.O.V. : Coefficient of variance

** Apparent true density includes closed pore volume

and the quantities mentioned above were calculated for both regions in order to determine capillary hysteresis. The flow controls of the porosimeter were adjusted so that each intrusion and extrusion stage took about five minutes, as was suggested by the manufacturer. A sample cell that has a base volume of 3×10^{-6} m³ and a stem volume of 2×10^{-6} m³ was used. For 3-D mercury intrusion experiments, ten 2.5×10^{-6} m³ samples of cookies and ten 2.5×10^{-6} m³ samples of bread were used. Interconnectedness of the pore structure was also studied by mercury porosimetry. For these tests only the desired two opposite faces of the sample were exposed to mercury intrusion. The other four faces were first covered with Duco cement, covered with paper, which had a pore diameter of less than 6 μ m (smallest pore diameter detected for bread and cookie samples), then taped. Mercury porosimetry was then performed to determine whether differences in intruded volume, pore size distributions and mean and median pore diameters existed when only unidirectional intrusion was allowed. For these unidirectional mercury intrusion experiments, fifteen samples of cookies and fifteen samples of bread were used.

Results and Discussion

Bulk density, apparent true density and porosity were the pore structure

parameters studied to assess uniformity of selected starch based food materials on a macroscopic level. These macroscopic pore structure parameters were further used to calculate the quantity of closed pores and to assess whether uniformity on the macroscopic level was an indication of uniformity on the microscopic level.

When bulk density, apparent true density and porosity for $0.04 \times 0.06 \times 0.01$ m³ samples of bread and $0.05 \times 0.06 \times 0.006$ m³ samples of cookies were determined (Tables 2 and 3), the largest coefficient of variance was found to be within 7%. However, samples of identical dimensions were found to lie in a wide range of weights (Tables 2 and 3). This fact first led to the questioning of the solid displacement technique with which bulk densities were determined. Since, the samples were geometrically uniform except for the surface irregularities, bulk volume could be determined from the dimensions of the sample. Bulk volume obtained from the dimensions was found to be 2% (at maximum) less than that found from the solid displacement technique. Thus, the difference in weight of dimensionally identical samples of the material in question was attributed to the existence of a different quantity of closed pores in each sample. As a result of this observation, the range of investigation was enlarged to samples of different dimensions so as to find out whether reproducibility on a macroscopic

Table 4. Comparison of mean bulk density, apparent true density and porosity for $0.05 \times 0.06 \times 0.006 \text{ m}^3$ samples with those calculated for samples of different sizes of butter cookies.

	Weight Range ($\text{kg} \times 10^{-3}$)	Bulk Density (kg/m^3)	Apparent* True Density (kg/m^3)	Porosity
** Samp. with Iden. Dim.	8.0-9.2	580	1310	0.55
*** Samp. of Var. Sizes	1.0-7.8	580	1330	0.57
**** % Diff.	-	-	1.50	3.50

* Apparent true density includes closed pore volume

** Samp. with Iden. Dim. : Samples with identical dimensions

*** Samp. of Var. Sizes : Samples of various sizes

**** % Diff. : Percentage difference

Table 5. Comparison of mean bulk density, apparent true density and porosity for $0.04 \times 0.06 \times 0.01 \text{ m}^3$ samples with those calculated for samples of different sizes of white bread.

	Weight Range ($\text{kg} \times 10^{-3}$)	Bulk Density (kg/m^3)	Apparent* True Density (kg/m^3)	Porosity
** Samp. with Iden. Dim.	2.8-3.4	130	1370	0.90
*** Samp. of Var. Sizes	0.5-4.2	130	1340	0.92
**** % Diff.	-	-	2.00	2.00

* Apparent true density includes closed pore volume

** Samp. with Iden. Dim. : Samples with identical dimensions

*** Samp. of Var. Sizes : Samples of various sizes

**** % Diff. : Percentage difference

level was accidental or if it applied to a wide range of sample sizes. Bulk density and apparent true density were measured for samples of different sizes which were in a weight range of 0.5×10^{-3} – $5.0 \times 10^{-3} \text{ kg}$ for bread and 1.0×10^{-3} – $10.0 \times 10^{-3} \text{ kg}$ for cookies. The mean bulk and apparent true density were found to be in the same order of magnitude for dimensionally identical samples and samples of different sizes in the weight range given above for both cookies and bread (Tables 2 and 4, 3 and 5). This implied that the level of reproducibility obtained for samples of identical dimensions was not accidental and uniformity on a macroscopic level were pursued down to a sample size corresponding to $0.5 \times 10^{-3} \text{ kg}$ of bread and $1.0 \times 10^{-3} \text{ kg}$ of cookies. However, under these conditions, porosity was expected to remain constant and should not have shown as much of a scatter as in Fig. 3 (especially for cookies), which was another indication of the existence of closed pores.

In order to calculate the quantity of closed pores, the true densities of compacted bread and cookie pellets were compared with the measured true densities of porous bread and cookie samples. The average true density of cookie pellets was measured as $1600 \text{ kg}/\text{m}^3$, compared to an average of $1300 \text{ kg}/\text{m}^3$ for the porous

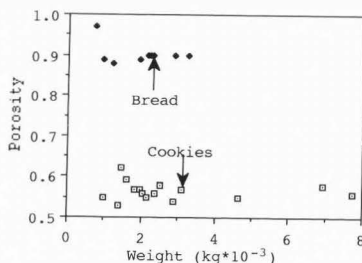


Fig. 3. Porosity of white bread and butter cookies for samples of different weights.

samples (Table 4). For bread, true density of the pellet was found to be $1500 \text{ kg}/\text{m}^3$, while apparent true density for the porous samples was found to be $1400 \text{ kg}/\text{m}^3$ (Table 5). This difference in true density of the pellets and the porous samples was a quantitative indication of the existence of closed pores. The porosity of the pellets was 0.03 which can be considered nonporous when compared to

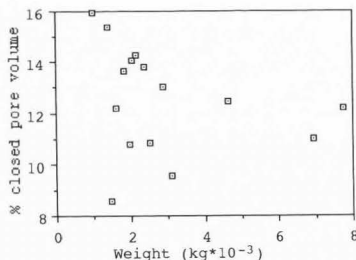


Fig. 4. Percentage closed pore volume in butter cookies for samples of different weights.

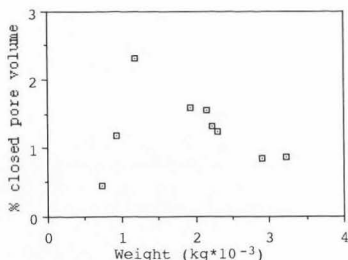


Fig. 5. Percentage closed pore volume in white bread for samples of different weights.

values for the original porous samples (0.6 for cookies and 0.9 for bread). When the percentage closed pore volume was calculated for each of the $0.04 \times 0.06 \times 0.01 \text{ m}^3$ bread samples and $0.05 \times 0.06 \times 0.006 \text{ m}^3$ cookie samples for which the weight, apparent true volume and bulk volume have already been measured, it was observed that the percentage closed pore volume varied greatly among samples of the same size (11% coefficient of variance for cookies and 21% coefficient of variance for bread), even though the samples were taken from the same batch of bread and cookies. This suggested that formation of closed pores was a random event using present processing techniques. The percentage closed pore volume was also calculated for bread and cookie samples of different sizes. The same random behavior was observed and no correlation with respect to weight could be detected (Figs. 4 and 5) which indicated that there is no representative sample size with respect to closed pores. The percentage closed pore volume in bread, a highly expanded product (porosity=0.9), was found to be between 1.0–1.5%, while it was found to be between 10–15% in cookies (porosity=0.6). Thus, the degree of expansion is a factor which may affect the formation of closed pores. However, the coefficient of variance of closed pore volume was higher for bread which suggests that the degree of expansion was not related to the uniformity on a microscopic scale. Thus, puffing mechanisms involved in the formation of closed pores need to be investigated. In order to support these quantitative results, SEM photomicrographs of bread and cookies were studied. The aim of these tests was to discriminate between the pore structure of cookies and bread and to obtain evidence about the existence of closed pores. For cookies, differences in pore structure caused by

the skin was also investigated. SEM photomicrographs of the cookie skin (Fig. 6a) showed much globular material which can be attributed to the presence of fatty material. In fact, cookies have a tough rather fatty skin. Most of the inner pores were blocked by the skin's compact fat layer and only a few pores were exposed to the environment. In such a texture, it is not surprising to find closed pores blocked by globular material (10–15% closed pore volume). Top and bottom skins were found to be the same qualitatively. On the other hand, SEM photomicrographs of the inner pore structure of cookies (Fig. 6b, c) showed that although the pores are larger internally, the globular material is still the dominant phenomenon. SEM photomicrographs of bread (Fig. 7) indicated that the structure of bread is very fragile with open and larger pores, as expected, since bread is a highly expanded product. This structure suggests that there should not be as many closed pores in bread, as is supported by the fact that the percentage closed pore volume is between 1.0–1.5%.

Mercury porosimetry data is limited to the prediction of pore sizes smaller than 200 μm . Preliminary porosimetry tests indicated that the smallest pore diameter for both bread and cookies is 6 μm which corresponds to a capillary pressure of $2.45 \times 10^5 \text{ Pa}$ (Hiçşmaz, 1990). Mercury intrusion results indicated that 65% of the available pore volume for cookies was formed of pores with diameters less than 200 μm , whereas only 16% of the available pore volume was in the detectable range for bread when the volume intruded is compared with the available pore volume measured by pycnometry. Therefore, the distributions and their means calculated from mercury porosimetry are only representative of the 16% and 65% of the

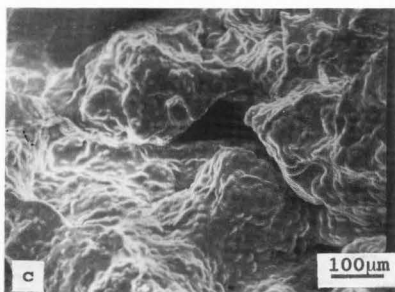
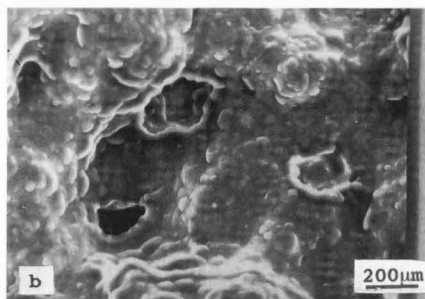
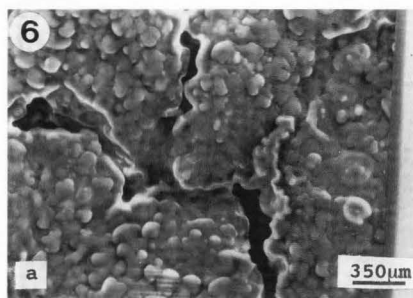


Fig. 6. Sample SEM photomicrographs of the pore structure of cookies
 a) the cookie skin
 b) sample sectioned in x-direction
 c) sample sectioned in z-direction.

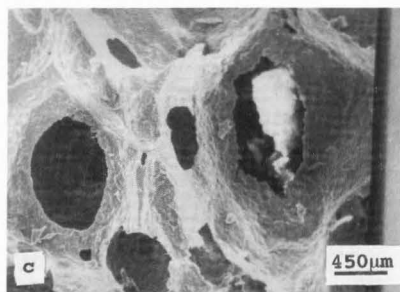
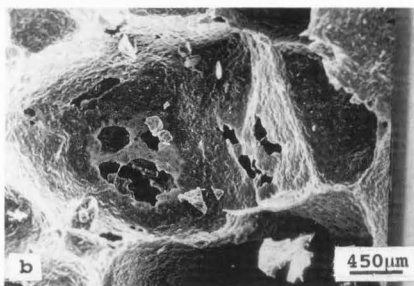


Fig. 7. Sample SEM photomicrographs of the pore structure of bread
 a) sample sectioned in x-direction
 b) sample sectioned in y-direction
 c) sample sectioned in z-direction.

Table 6. Comparison of intrusion and extrusion results for one kilogram of butter cookies and white bread.

	Volume of Mercury Intruded				Volume of Mercury Extruded				Volume of Mercury Entrapped			
	(m ³ /kg)×10 ³				(m ³ /kg)×10 ³				(%)			
	Max	Min	Mean	C.O.V (%)	Max	Min	Mean	C.O.V (%)	Max	Min	Mean	C.O.V (%)
Cookies	0.72	0.62	0.67	6	0.14	0.09	0.11	26	84	81	83	2
Bread	1.26	1.05	1.13	8	0.06	0.04	0.05	19	95	90	94	3

Max : Maximum

Min : Minimum

C.O.V : Coefficient of variance

available pore volume for bread and cookies, respectively. In other words, the porous media chosen have different ranges of pore size distributions, and only a small range of overlap could be studied by mercury porosimetry. For pores larger than 200 μm , image analysis together with quantitative stereology have to be used (Dullien et. al., 1969/70; Dullien and Mehta, 1971/72; Dullien and Dhawan, 1973; Dullien and Dhawan, 1974; Dullien and Dhawan, 1975; Dullien, 1979). But, in infusion, even pores in the diameter range of 6-200 μm offer little resistance to the flow of oils and oil based materials owing to low values of surface tension and contact angles of less than 90 degrees (Hiçşmaz, 1990). Therefore, there was no point in analyzing pore sizes above 200 μm for infusion purposes.

Mercury intrusion and extrusion results were compared in order to assess capillary hysteresis. Results obtained are reported in Table 6 and typical intrusion and extrusion curves for a cookie and a bread sample are given in Fig. 8. About 95% of intruded mercury is entrapped in bread samples, while 80% mercury entrapment is encountered in cookies. This indicates that both bread and cookies contain pores where narrow pore segments are followed by segments which are larger in diameter. However, by the straight capillary model these larger pore segments are treated as having the same diameter as do the narrowest pore segment to which they are connected. Thus, results obtained for pore surface and pore population distributions by using this model were meaningless (Hiçşmaz, 1990). The fact that mercury entrapment is less in cookies than in bread can be attributed to bread being a highly expanded product containing very large pores connected by narrow necks. The cellular structure of bread suggested by SEM (Fig. 7) is the qualitative support of this phenomenon. As can be observed in

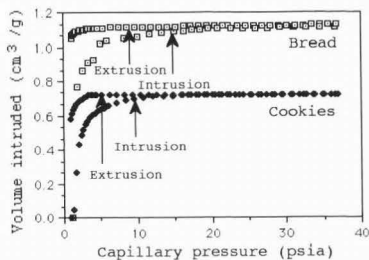


Fig. 8. Comparison of intrusion and extrusion curves based on one gram of butter cookies and white bread.

Table 6, the coefficient of variance for the volume of mercury extruded is very large. This is due to the fact that the small-large-pore segment assembly in different samples are expected to be different as was observed in estimating the percentage closed pore volume. Thus, the formation of a small-large-pore segment assembly is also a random phenomenon which needs to be investigated in terms of mechanisms involved in puffing.

Results obtained on high levels of capillary hysteresis indicate that infusion of oil based liquid food materials containing particulate solids may pose problems if the size of particulate solids present are in the order of the diameter of the smallest pore segments. In such cases, particulate solids will be filtered out in these pore segments and will never reach the segments with larger diameters. Thus, the product will not be infused uniformly i.e., the suspended solids in the oil based food suspension are filtered out, while the fat

Table 7. Comparison of 3-D mercury intrusion results with unidirectional mercury intrusion results based on volume intruded per kilogram of butter cookies.

	Max (m^3/kg) $\times 10^3$	Min (m^3/kg) $\times 10^3$	Mean (m^3/kg) $\times 10^3$	C.O.V. (%)	Mean Pore Vol. Int. (%)
3-D	0.72	0.62	0.67	6	65
x-dir	0.70	0.64	0.67	5	65
y-dir	0.69	0.62	0.66	7	64
z-dir	0.69	0.64	0.67	5	65

Max : Maximum
Min : Minimum
C.O.V. : Coefficient of variance
Vol. Int. : Volume intruded

Table 8. Comparison of 3-D mercury intrusion results with unidirectional mercury intrusion results based on volume intruded per kilogram of white bread.

	Max (m^3/kg) $\times 10^3$	Min (m^3/kg) $\times 10^3$	Mean (m^3/kg) $\times 10^3$	C.O.V. (%)	Mean Pore Vol. Int. (%)
3-D	1.26	1.05	1.13	8	16
x-dir	1.25	1.08	1.17	9	16
y-dir	1.23	1.03	1.13	7	16
z-dir	1.23	1.07	1.15	9	16

MAX : Maximum
Min : Minimum
C.O.V. : Coefficient of variance
Vol. Int. : Volume intruded

phase readily fills in the accessible larger pores (Barrett and Ross, 1990; Barrett et. al., 1990). However, this is not due to the effect of pore size only, but particulate solids in the food suspension also tend to form agglomerates during deposition. Since filtration is a physical phenomenon, the only way to prevent this is to produce starch based entities with controlled pore size distributions representing large enough pore sizes which would prevent solid deposition. Moreover, techniques which would decrease the affinity of the specific particulate solid in the suspension towards the starch based solid described here should be investigated. One of such techniques which could be studied is the addition of food-grade cohesives towards the particulate solids in question into the initial recipe of the starch based porous material to be infused. However, this speculation needs much further investigation.

Unidirectional mercury intrusion experiments performed in x-, y- and z-directions for bread and cookies revealed that the same amount of pore volume is filled with mercury as in the 3-D experiments (Tables 7 and 8). This indicates that the starch based porous media studied is so highly interconnected that intrusion in only one direction is enough to literally flood the media even with mercury which is nonwetting (contact angle=140 degrees) and has a much higher surface tension (480×10^{-3} N/m) than oils and oil based food materials (Higassmaz, 1990). Even when the fluid is introduced in one direction, flow takes place three

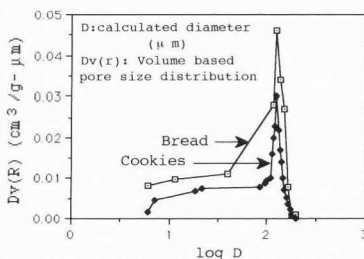


Fig. 9. Volume based pore size distribution for one gram of butter cookies and white bread.

dimensionally. The straight capillary model is readily applicable in such cases (Chatzis and Dullien, 1977). However, in order to get a detailed picture of pore structure which accounts for capillary hysteresis, a one-dimensional (1-D) network model is suggested.

As seen in Fig. 9, the differential volume based pore size distribution curve for bread was wider than that for cookies. This can be attributed to the fact that large pores are predicted to be much smaller than they are due to the straight capillary model, which assumes that larger pore segments are always followed by smaller ones. Moreover, as was mentioned earlier, this differential data represents

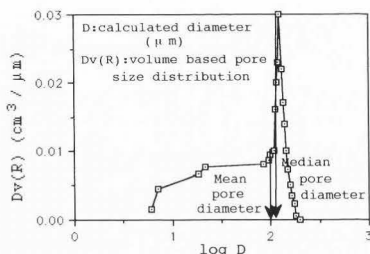


Fig. 10. Mean and median pore diameters of the volume based pore size distribution for one gram of butter cookies.

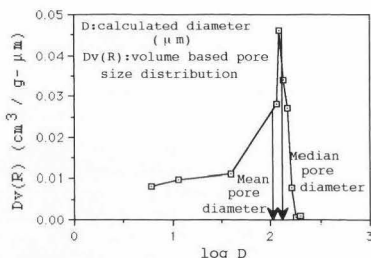


Fig. 11. Mean and median pore diameters of the volume based pore size distribution for one gram of white bread.

only 16% of the pore volume which most likely also contains pores with diameters larger than 200 μm that are falsely detected. Volume based pore size distribution curves (Fig. 9) showed the same characteristics for bread and cookies. In other words, for both bread and cookies there are so many large inner pores which are preceded by smaller surface pores that most of the pore volume is intruded when the smallest pore size is about 60 μm (corresponding to about 75% of the intruded pore volume (Fig. 8)) for bread and when the smallest pore size is about 50 μm (corresponding to about 50% of the intruded pore volume (Fig. 8)) for cookies. This conclusion is semi-quantitatively supported by the histograms shown in Figs. 10 and 11 and also by the random distribution of pore sizes in Figs. 6 and 7. However, since Fig. 8 is the most important evidence for capillary hysteresis, a wide distribution of smaller pore sizes proves that pores smaller than 60 μm for bread and 50 μm for cookies exist in small quantities and towards the center of the samples exposed to 3-D mercury intrusion.

To assess variability among samples, mean and median pore diameters for the differential volume based distribution were used. Mean and median pore diameters for a typical cookie sample and a typical bread sample are given in Figs. 10 and 11. The mean pore diameter is the weighted arithmetic average of the distribution function, while the median pore diameter is the diameter at which an equal volume of mercury is intruded into larger and smaller pores than the median. The coefficients of variance for mean and median pore sizes of cookies were found to be very high when compared to those for bread (Table 9). This may be attributed to globular material of different sizes randomly distributed within the pore structure of cookies as was observed on

the sample SEM photomicrographs (Fig. 6). Thus, each sample is bound to contain a variety of globular material which may contribute to variability on a microscopic level.

Comparison of volume based intrusion and extrusion distributions is given in Table 9. Owing to capillary hysteresis, volume based extrusion distributions both for bread and cookies have much smaller mean and median pore diameters. In other words, larger pores which are not on the surface contain entrapped mercury. As in the case of intruded volume of mercury, the coefficient of variance was very high both for bread and cookies due to the random distribution of pore segments with different diameters.

In order to support the results on the presence of pores with diameters larger than 200 μm , pore sizes detected by SEM were measured and the results based on the percentage of pores corresponding to a measured diameter (representing 60 pores for cookies and 50 pores for bread samples) are given in Figs. 12 and 13. It can be seen in Fig. 6 that no pores with diameters greater than 200 μm were detected in the SEM photomicrographs for cookies, whereas 30% of the pore diameters measured for bread (Fig. 7) were greater than 200 μm . The arithmetic mean of these pores were calculated as 92 μm for cookies which is close to the value of 90 μm obtained by mercury porosimetry (Table 9). However, with bread, the arithmetic mean of the pore diameters measured from SEM photomicrographs was found to be 153 μm in comparison with 122 μm obtained by mercury porosimetry (Table 9). These results are in concordance with the fact that only 16% of the pore volume of bread is within the mercury porosimetry range.

Conclusions

Both the highly expanded bread

Table 9. Comparison of mean and median pore diameters of volume based intrusion and extrusion distributions for one gram of butter cookies and white bread.

	INTRUSION								EXTRUSION							
	Mean Pore Diameter (μm)				Median Pore Diameter (μm)				Mean Pore Diameter (μm)				Median Pore Diameter (μm)			
	Max	Min	Mean	C.O.V (%)	Max	Min	Mean	C.O.V (%)	Max	Min	Mean	C.O.V (%)	Max	Min	Mean	C.O.V (%)
Cookies	133	110	122	8	152	132	142	7	70	33	53	29	73	29	54	3
Bread	104	75	90	15	119	66	98	25	74	44	65	22	72	44	64	21

Max : Maximum
 Min : Minimum
 C.O.V : Coefficient of variance

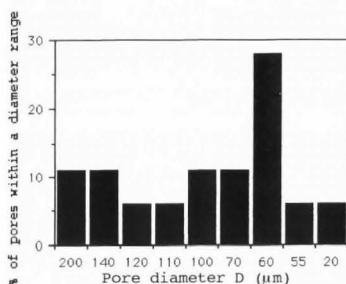


Fig. 12. Histogram for percentage of pores located within an observed diameter range as measured from SEM photomicrographs for butter cookies.

samples and the relatively compact cookie samples contain closed pores. Formation of these closed pores is a random event which varies to a great extent among samples. Thus, uniformity among samples of the same starch based food product on the macroscopic level with respect to bulk density, true density and porosity is not an indication of uniformity on a microscopic level in terms of closed pores and small-large pore segment assemblies.

It is evident that a complete picture of the pore size distribution of bread and cookies cannot be obtained by mercury porosimetry only, since both materials contain pores larger than 200 μm which are outside the porosimetry range. Therefore, for starch based porous foods which have a porosity of 60-90%, mercury porosimetry should be used in combination with image analysis after which the data obtained would be analyzed by quantitative stereology.

Mercury intrusion and extrusion

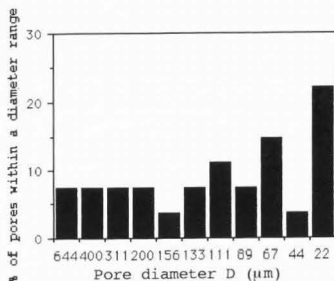


Fig. 13. Histogram for percentage of pores located within an observed diameter range as measured from SEM photomicrographs for white bread.

results show that capillary hysteresis is a major phenomenon for both bread and cookies. The assembly of small-large-pore segments are distributed randomly within the porous matrix. Thus, the straight capillary model cannot predict the pore size distributions correctly and network modeling should be used to simulate these random structures after obtaining the necessary data through porosimetry and image analysis. However, both bread and cookies are made up of a highly interconnected pore structure which indicates that a 1-D network model can yield a more realistic picture of the pore structure when needed.

In the light of these pore structure studies, it is worthwhile to study the mechanisms involved in pore formation so as to be able to understand the reasons behind the formation of closed pores and to be able to produce puffed starch based foods with controlled pore size distributions.

Acknowledgements

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Discussion with Reviewers

S.H. Cohen: You state in the "Results and Discussion" section that "differences in the weight of unidimensionally identical samples ... were attributed to the existence of a different amount of closed pores in each sample." Why would closed pores -- rather than porosity or pore volume in general -- affect sample weights (and therefore sample density)?

Authors: Definition of the apparent true density of the sample which considers the closed pore volume as a part of the solid volume is;

$$\text{Apparent true density} = \frac{\text{Weight}}{\text{Apparent solid vol.}}$$

Let us consider two porous samples which have the same bulk volume and prepared from a homogeneous mixture of the same ingredients, but one contains closed pores and the other does not. The sample which does not contain closed pores weighs more, since it contains more solids in the same bulk. When the apparent solid volume of these two samples are measured by pycnometry, the solid volume for the sample which does not contain closed pores appears to be less, since the Nitrogen gas used in pycnometry cannot penetrate these closed pores. Thus, the closed pores are falsely detected as a part of the solid in the porous sample. Our measurements indicate that the effect of the presence of closed pores on the sample weight and apparent solid volume compensate each other to yield a coefficient of variance in the order of 1.5-2.0% (Tables 2 and 3) in apparent true density, while the coefficient of variance is between 5.5-9.0% (Tables 2 and 3) with respect to the sample weights. On the other hand, porosity is defined as;

$$\text{Porosity} = \frac{\text{Bulk vol.} - \text{Apparent solid vol.}}{\text{Bulk vol.}}$$

Thus, porosity is an intensive property and is in a way a normalization of the pore volume with respect to the bulk volume. In this definition, presence of closed pores affect only the apparent solid volume. For samples with porosities between 60-90%, the apparent solid volume constitutes only 10-40% of the bulk volume. Therefore, the effect of closed pores on porosity is expected to be negligibly small in the porosity range studied. This is supported by the fact that the coefficient of variance for porosity is between 0.5-1.5% (Tables 2 and 3). However, although the coefficient of variance is not high, a scatter in porosity was observed (Fig. 3), especially for cookies which contain more closed pores (10-15% of the available pore volume).

S.H. Cohen: Unidirectional and 3-D intrusion experiments yielded the same values for pore volume in both cookie and bread samples due to the high degree of interconnectedness in these materials. Since interconnected samples are not necessarily isotropic, did you observe any differences in the measured pore size distributions?

Authors: By the help of the

unidirectional mercury intrusion experiments, we found that both bread and cookies possess highly interconnected pore structures (Tables 7 and 8), but with the experimental techniques we used, it was not possible to conclude whether the materials were isotropic or not. First of all, the pore size distributions were obtained by mercury porosimetry were representative of only about 16% of the total pore volume for bread and 65% of the total pore volume for cookies. Moreover, although the coefficient of variance among samples was between 6-8% with respect to mercury intrusion (Table 6), the coefficient of variance obtained for the mean and median diameters of the pore size distribution curves was found to be between 7-25% (Table 9). The coefficient of variance obtained for the mean and median pore diameters was even more striking (20-35%) for mercury extrusion (Table 9). For such variability on the microscopic scale, no conclusions on isotropicity with respect to pore size distributions can be reached before a detailed pore structure analysis is carried out by means of quantitative stereology and network modeling. However, we believe that it should be possible to obtain experimental evidence on isotropicity by combining our unidimensional experimental technique with image analysis.

S.H. Cohen: You attribute the high proportion of closed pores in cookies to the presence of fat globules that block channels. Cookies and bread vary in many ways in addition to composition, especially in terms of their overall pore structure (i.e. bread is a cellular "honeycomb" while cookies are not) and in the mechanism of pore formation. Could you speculate further on why pores in cookies may be less accessible than those in bread?

Authors: Vapor induced puffing is the process which governs the formation of pore structure. However, mechanisms involved in pore formation has not been entirely understood due to the lack of information on the physicochemical behavior of the ingredients involved in vapor induced puffing. It is evident that fermented and unfermented dough behave differently towards vapor induced puffing. In bread, a fermented dough product, pore formation is initiated by the gas cells due to fermentation before baking. Then, during baking, vapor pressure build-up also occurs, in addition to the pressure build-up due to entrapped carbon dioxide in the gas cells. The starch granules undergo gelation and form an elastic gel due to interaction with the gluten in flour. However, when the vapor pressure within the gas cells is enough to overcome the gel strength, vapor and carbon dioxide

break the structure through the mechanically weak points in the starch-gluten gel network and escape making their way through these weak points. Thus, the pressure in the gas cells decreases also causing the temperature to decrease, which in turn, causes the walls of the cells to solidify. Therefore, the gas cell formation before baking causes noninterconnected large pores to form which are easily interconnected to each other during baking forming a highly interconnected network of large pores with fragile membrane-like walls. On the other hand, in unfermented dough, pore formation depends only on the vapor pressure build-up during baking, thus such dough products do not contain an initial network of gas cells to be interconnected during the baking stage. Moreover, if the dough contains sugar and fats and/or lipids in addition to the flour, vapor induced puffing does not only depend on the interactions of gluten and starch to form a gel network, but the physicochemical interactions between all these components going through phase transitions become important. Moreover, although the dough may be homogeneous on a macroscopic level, it is not expected to be uniform on the microscopic level with respect to the interactions between gluten, starch granules, fat globules and sugar. It looks like the globular fat and lipid material do not respond to phase transitions in the same manner and same rate as the gluten-starch gel network, thus remaining as globular material blocking the pore network formed during vapor induced puffing.

S.H. Cohen: Is mercury intrusion porosimetry really a useful technique for highly porous materials like bread when so much of the structure (85%) cannot be analyzed by this technique?

Authors: Mercury porosimetry for highly porous materials may not be a useful technique when an entire picture of the pore structure is required. However, if an entire picture is required, SEM is not enough either, since very large and very small pore segments coexist randomly in starch based food materials as proved by mercury porosimetry results. Thus, to obtain an entire picture of the pore structure, a combined approach using mercury porosimetry and image analysis followed by quantitative stereology techniques and network simulation of the experimental data, is necessary.

R. Chinnaswamy: Were three tappings of the glass container sufficient to obtain a true bulk volume of the products? How did you optimize your number (three) of tapping procedure?

Authors: With no tappings, a coefficient of variance of 10% was obtained for ten measurements of the bulk density of

rapeseeds in the 0.14 m³ glass container. With a single tapping, the coefficient of variance for ten measurements decreased to about 6%, with two tappings, it decreased to about 3%. With three tappings, the coefficient of variance for ten measurements decreased to about 1% and no appreciable decrease in the coefficient of variance was observed by a further increase in the number of tappings. Thus, the bulk density measurements were carried out at three tappings.

R. Chinnaswamy: Mercury intrusion and extrusion experiments were done at high pressures. Is this expected to break some fragile closed and open pores in the product? Was there any dry matter in the extrudates?

Authors: Mercury porosimetry showed that 75% of the intruded pore volume is formed of pores with diameters in the 60-200 μ m range for bread and 50% of the intruded pore volume is formed of pores with diameters in the 50-200 μ m range for cookies. Moreover, only 16% of the available pore volume is in the detectable range of mercury porosimetry for bread, while 65% of the available pore volume can be studied by mercury porosimetry for cookies. Therefore, in order to study the range of pores detectable by mercury porosimetry we had to start at the lowest possible limit of vacuum pressure (6.6 Pa) and this was only possible with predried solid materials as described in the section titled "Preparation of Starch Based Solids" in "Materials and Methods". Preliminary mercury porosimetry tests showed that intrusion proceeded until 2.45×10^5 Pa, then no intrusion was observed until 2.7×10^5 - 3.0×10^5 Pa pressure range. Within this pressure range, a sudden increase in intruded volume occurred, and the test samples did not remain intact. Thus, porosimetry tests were carried out until 2.45×10^5 Pa. Although some collapse in pore structure may have occurred, it is trivial when compared to what was observed at the 2.7×10^5 - 3.0×10^5 Pa pressure range.

R. Chinnaswamy: Most of these porous products contain gelatinized starch which is expected to absorb water from pastes pumped-in. This will contribute to collapse of the open and closed porous cells in the products. What is a typical α for pumpable paste materials? Describe their typical chemical compositions and their functions.

Authors: We used only chocolate syrup as the food suspension during our vacuum infusion studies for which the results have not been published, yet. Chocolate syrup contained about 25% moisture, 15% fat, 5% protein and 50% carbohydrates.

The absorption capacity of bread and cookies towards chocolate syrup and the pure lipid phases were also studied. The results on these wettability studies are in press in the "J. Food Eng". However, extensive information on vacuum infusion can be found in literature (Barrett and Ross, 1990; Barrett et. al., 1990).

R. Chinnaswamy: Give examples of porous cereal products that are filled with pumpable pastes which are available in markets.

Authors: Our vacuum infusion studies as well as Barrett and coworkers (Barrett and Ross, 1990; Barrett et. al., 1990) were directed towards producing calorically dense rations which so far we did not see any available in the markets. However, it should be made clear that infused products are different from breakfast cereals obtained by co-extrusion. In co-extrusion, an intentional pore is made when filling in the paste, thus the filled porous cereal product is obtained in a single process, where the puffed cereal part still contains empty pores. On the other hand, vacuum infusion is directed towards already manufactured cereal products in which the available pore space is filled with the paste to obtain calorically dense rations.

D. Bertrand: As mentioned in the introduction, the purpose of the work was to appreciate the ability of foodstuffs to absorb a high calorie liquid. Is there currently any evidence that the porosity measurements are correlated to this ability?

Authors: In fact, it was concluded that the macroscopic pore structure parameter, porosity, cannot be correlated with the ability of porous food products to be infused uniformly, since high porosity is not an indication of a controlled pore size distribution which is supported by the fact that bread samples with 0.90 porosity contain pores as small as 6 μm . For infusion uniformity with food suspensions which contain particulate solids with particle sizes ranging between 5-50 μm (Barrett and Ross, 1990; Barrett et. al., 1990), the controlling parameters are; (a) the pore sizes which need to be larger than the particle size in the food suspension to overcome filtration, (b) the affinity of the particulate solids towards the starch based pore walls and towards each other to overcome deposition and agglomeration.

D.J. Gallant: During drying, what was the reduction rate of bread samples? And, as a consequence, what was the reduction of the pore sizes? Could you explain why bread samples needed only 3 hours drying at 65°C and cookies, 72 hours?

Authors: It is true that drying may

affect pore sizes, but the starch based materials used for infusion need to be predried as well, since infusion is a vacuum process which requires predried materials to be able to obtain adequate vacuum. Therefore, since we directed our studies towards the pore structure which would affect infusion uniformity, we did not take any data during the drying stage. Moreover, drying is not expected to affect the pore structure of cookies, since cookies are originally quite low in moisture content (4.5% moisture). However, with bread, an originally high moisture content (40% moisture) material, drying may have changed the pore size. Both bread and cookie samples were dried at 65°C for 72 hours, but since bread contains about 40% moisture, an initial drying period for 3 hours at 65°C was applied to bread slices in order to obtain uniform samples with required dimensions.

D.J. Gallant: In your paper, the SEM was used in order to study qualitatively the 3-D of the pores viewed in your two samples. Suppose you need to measure quantitatively samples porosimetry by image analysis. Would you take SEM picture (deep depth of field) or pictures from light microscopy (low depth of field)? Image analysis on SEM needs preferably flat images (that is not the case in Fig. 7) and as well as possible without backscattered electrons. When sample is somewhat translucent (due to backscattered electrons) as on Fig. 9 and show very deep depth of field, it should be very difficult to appreciate the true porosity, (especially with an image analyzer). Did you try to resolve this problem? Did you measure porosity of such products by this way and in this case, what was the correlation degree with the pycnometer measurements. All suggestions are welcome.

Authors: We used SEM photomicrographs especially to obtain visual evidence on the presence of closed pores. therefore, on purpose, we took the photomicrographs by keeping the samples in tilted position so as to add a depth to the picture in order to see whether we could observe what causes the closed pore structures. Moreover, if we decided to analyze the pore structure quantitatively by means of SEM photomicrographs, 20 for cookies and 15 for bread would have been absolutely inadequate. Also, since bread and cookies contain pores varying in sizes between 6-600 μm , each sample should have been photographed at a variety of magnifications. For example, although mercury porosimetry indicates that 35% of the pore volume in cookies should be formed of pores larger than 200 μm , we could not observe any of these pores in our photomicrographs. If pore structure

were to be studied by SEM, then first the representative number of photomicrographs should have been determined by increasing the number until porosity calculated by the help of quantitative stereology approaches the porosity obtained from pycnometry.

Therefore, SEM photomicrographs is not recommended for quantitative pore structure analysis. However, optical means involving a video camera coupled to a computer with the necessary hardware interface has successfully been used by Barrett and coworkers (Barrett and Ross, 1990) to study the pore structure of food materials and by Dullien and coworkers (Dullien et. al., 1969/70; Dullien and Mehta, 1971/72; Dullien and Dhawan, 1973; Dullien and Dhawan, 1974; Dullien and Dhawan, 1975; Dullien, 1979) to study the pore structure of petroleum-bearing rocks.